OCO (Orbiting Carbon Observatory) -2

Spectroscopic needs for OCO-2

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Revision History

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1 Introduction

1.1 Scope and Background

This document is intended to provide an overview of the v4.2 ACOS/OCO-2 absorption coefficient (ABSCO) tables, key features and issues and potential directions for future research.

The ACOS/OCO-2 ABSCO tables are "lookup tables" that supply cross section values for absorbing gases in the Level 2 algorithm (L2) retrieval process. They record molecular absorption cross-sections over the range of relevant wavelengths, temperatures, and pressures in units of cm^2/mol for the gases O_2, H_2O, and CO_2. During the L2 generation process the retrieval algorithm computes atmospheric absorption at each relevant temperature, pressure, and wavelength using linear interpolation. Successive versions have refined these tables by incorporating new laboratory results and theoretical models for increasingly accurate absorption coefficients. ABSCO tables are released together with each major build of the OCO-2 Level 2 algorithm. ABSCO v4.2 tables were used for the ACOS B3.5 Level 2 retrievals.

The tables can be computed at a spectral resolution of 0.002 cm^{-1} (required for validation of the tables using high resolution laboratory spectra) but the current L2 retrieval code uses a spectral resolution of 0.01 cm^{-1}.

1.2 Document Overview

Section 2 describes the absorption cross-section computation, while Section 3 describes the format of the ABSCO HDF files. Section 4 provides an overview of the remaining challenges and plans to address them.

1.3 Data Usage Policy

The OCO-2 ABSCO tables are provided freely to the public, on request. We request that when publishing using the tables, please acknowledge NASA and the ACOS/OCO-2 project.

- Include OCO-2 as a keyword to facilitate subsequent searches of bibliographic databases if it is a significant part of the publication
- Include a bibliographic citation for the tables. The most relevant citation currently is Thompson et al. (2012).
- We recommend sending courtesy copies of publications to the OCO-2 Project Scientist, Michael.R.Gunson@jpl.nasa.gov.

2 Absorption cross section computation

This section describes the studies providing line parameters for each of the main absorbing gases. Due to the modular nature of the ABSCO calculation, different bands rely on different codebases to compute the absorption cross sections. In summary, the LABFIT codebase from (Benner 2011) provides CO_2 cross sections. This implements databases from (Benner 2011) and (Devi 2007) for 2.0um and 1.6um CO_2, respectively. The procedure and modeling assumptions of this

approach are detailed at greater length in (Thompson 2012). A line mixing codebase from (Tran 2008) computes the major isotope of O_2. We use the ABSCOI codebase, a routine adapted from the GFIT software package in use by the Total Column Carbon Observing Network (TCCON, Wunch 2010), for the minor isotopes of O_2 and all CH_4 and H_2O lines. A flowchart showing the principal line list sources and the computation strategies for each line appears below in Figure 1.

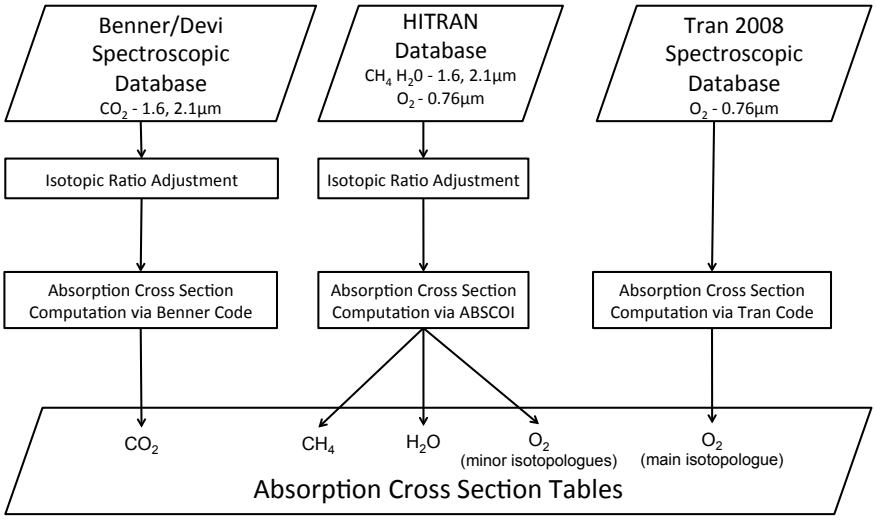

Figure 1. Absorption coefficient calculation processing and sources.

In v4.2, the table format is a four-dimensional array to accommodate an additional "foreign broadener gas" dimension. This allows cross sections to be parameterized by temperature, pressure, and the volume mixing ratio of one other atmospheric gas. All tables are provided in this 4D format, though the calculations only incorporate broadening by H_2O of O_2 and CO_2. CH_4 tables using the HITRAN line list are now also available; they are computed over both CO_2 spectral windows. The temperature range has 17 levels and is intended to cover extremely low (terrestrial) temperatures. Table 1 below gives more detailed information on several key parameter sources.

Note that scaling factors are applied to the v4.2 absorption cross sections within the B3.5 Level 2 algorithm. O_2 cross sections are rescaled by a factor of 1.0125, CO_2 cross sections in the strong (2.06 μm) band are rescaled by 0.9946 and CO_2 cross-sections in the weak (1.6 μm) band are rescaled by 1.0038. The O_2 scaling factor was chosen in order to bring the mean retrieved surface pressure into agreement with ECMWF values. The CO_2 scaling factors were chosen in order to minimize disagreement with XCO_2 values from the Total Column Carbon Observing Network (TCCON) and to provide consistency between single-band CO_2 retrievals. The ABSCO HDF files themselves contain *unscaled* cross sections.

Table 1: ABSCO v4.2 Parameter Sources

	0.76µm O_2	1.61µm CO_2	2.06µm CO_2	H_2O
Spectral range	12745-13245 cm^{-1}	4700-6500cm^{-1}	4700-6500cm^{-1}	12745-13245cm^{-1} 4700-6500cm^{-1}
Spectral resolution	0.01cm^{-1} or 0.002cm^{-1}	0.01 cm^{-1} or 0.002cm^{-1}	0.01 cm^{-1} or 0.002cm^{-1}	0.01 cm^{-1} or 0.002cm^{-1}
Position	Long (2010), Long (2011)	Devi (2007)	Benner/Devi (2011)	Gordon (2012), Rothman (2010)
Intensities	"	"	"	"
Air-widths	Tran (2008)	Predoi-Cross (2009)	"	"
Air-shifts	Brown (2009) Robichaud (2008a) Predoi-Cross (2008)	Devi (2007b)	"	"
Temp. dep.	Brown (2000)	Predoi-Cross (2009)	"	"
Line shapes	Voigt / Galatry	Speed-dependent Voigt	Speed-dependent Voigt	Voigt
Isotopologue abundance	Rothman (2009)[1]	Rothman (2009)	Rothman (2009)*	Rothman (2009)
H_2O broadening	Drouin (2013)	Sung (2009)	Sung (2009)	-
Air-Line mixing	Tran (2008)	Devi (2007)	Benner/Devi (2011)	-
" Temp. dep.	Tran (2008)	-	-	-
Speed dep.	-	Devi (2007)[1]	Benner/Devi (2011)	-
Continuum	CIA via Tran (2008)	-	Mlawer (2012) *	Mlawer (2012) *

*see text for further details

0.76um O_2 Detail

The O_2 main isotopologue uses intensity and position parameters from new Cavity Ring Down Spectroscopy measurements (Long et al. 2010). The use of these parameters significantly reduces surface pressure error, while increasing yield.

Note that the (Long 2010) air-broadened half widths were *not* incorporated. The reason is that we found these parameters to be highly coupled with our line mixing strategy so that any change from the values provided in (Tran 2008) degraded performance. For consistency, we retain a Voigt line shape with widths and line mixing model exactly the same as in (Tran 2008). Those widths are based on a parameterization first found in (Yang 2005). Pressure shifts are from previous work by from (Robichaud 2008b) and (Predoi-Cross 2008) found in HITRAN 2008, with modifications to the R Branch by (Brown 2009). Minor transitions and isotopologues are computed using measurements from (Long 2011). The Galatry line shape was used for these minor lines, since narrowing parameters are available for lines in the Long et al. list. We

supplemented them with a few additional Voigt-profile lines from the HITRAN 2008 database to cover all remaining weak O_2 lines in the entire 12850-12900cm^{-1} window.

Parameters for broadening of O_2 by H_2O come from the study by Drouin et al. (2013).

Previous work (Butz 2010, Thompson 2012) has used an *ad hoc* rescaling of cross sections to reduce systemic surface pressure error. As stated previously, a rescaling factor of 1.0125 was used in this case to counter a surface pressure bias evidenced in the retrievals.

1.6μm and 2μm CO_2 Detail

The CO_2 bands use line parameters and mixing models derived from studies by Benner/Devi (2011) and Devi (2007). Additional detail on validation experiments for these databases, which are used in all line list versions after v4.0, are found in Thompson et al. (2012). The computation incorporates a speed dependent line profile with tridiagonal line mixing. Parameters for foreign broadening of CO_2 by H_2O come from studies by Sung et al (2009). This study treated the 4.3μm band only. However, it is likely that these can be safely extrapolated to the other bands as well, and we favor this approach until additional direct laboratory data is available.

We modify the HITRAN 2008 isotopologue abundances slightly in the CO_2 band. These abundances are typical for measurements taken at sea level, but higher in the atmosphere CO_2 fractionation effects can modify the apparent abundances. Specifically, the 628 isotopologue abundance is increased by a factor of 1.04 to account for these apparent differences, and for the intrinsic uncertainty in band strength as measured in the laboratory. This factor was derived empirically from tests using the TCCON network of ground based, upward-looking FTS stations.

We note one final difference between the reference databases and our computed absorption coefficients. We found it necessary to incorporate an additional continuum absorption in the 2.06 um CO_2 band which takes the shape of two Gaussian distributions centered at 4853.5 and 4789 wavenumbers, with respective standard deviations of 10 and 8 wavenumbers and intensity scalings of 2.1e-24 and 4.2e-25, respectively (this is the intensity at 1 Atm, but absorption at other levels scales in proportion to pressure). These parameters were set to minimize error in retrievals with TCCON uplooking FTS spectra.

H_2O Detail

We incorporate revised H_2O line parameters from Gordon et al. [2012] for the 2μm region. It is likely that some or all of these parameters may become the standard for HITRAN 2012. We compute the H_2O Continuum using the AER MT_CKD codes (Mlawer et al., 2011). 1.67υm parameters are provided by HITRAN 2008, with the exception of a single line near 6290cm^{-1} that we modified empirically by hand. This procedure, performed with the help of Dr. Iouli Gordon, reduced a prominent residual that we noted in both TCCON and GOSAT atmospheric retrievals. New line parameters from the HITEMP database (Rothman et al. 2010) have been used for weak water lines in the Oxygen A Band. Another change from the previous ABSCO version is that the line wing cutoff for H_2O lines has been reduced to 25cm^{-1} for consistency with the assumptions of the MT_CKD continuum model. This was a minor error in previous versions, and it is unlikely to have significantly impacted retrieval results. Finally, the continuum itself has been revised. We use an unofficial modified version of the AER MT_CKD continuum (Mlawer et al. 2012), supplied for testing purposes only by Eli Mlawer. This increases the continuum slightly

over the previous version of the AER MT_CKD model in the OCO-2 spectral intervals. There is no absolute consensus yet on the continuum level in the 2.06 micron band. This revision offers a conservative compromise between the previous continuum and new measurements by Ptashnik et al. (2011). The revised MT_CKD also falls relatively close to new measurements by Mondelain et al. (2013).

Overall we find that the combination of these changes improves the spectrum fit quality for typical TCCON and GOSAT retrievals.

3 HDF5 Format Specification

The ABSCO tables are provided in an HDF5 format. The table is a 4D structure indexed in the following order:

- pressure levels 1 to N_{pres}
- temperature levels from 1 to N_{temps}
- foreign broadener vmrs from 1 to N_{vmrs}
- frequencies from 1 to N_{freqs}

In general, each table models one absorbing gas and up to one foreign broadening gas (here, always H_2O). We refer to the abosrber's HITRAN gas index value with the symbol Q_{abs} and its HITRAN isotope index as R_{abs}. The foreign broadener index is $Q_{brd.}$

The HDF file is has the following format:

– **File:** The top-level file object represents a collection of one or more absorber gas cross sections that have been computed for a common spectral range and set of atmospheric conditions. The file contains top-level attributes:
  - version: a version string describing the table release
  - addl_ident: a special identifier string, if any
  - gas_name: a string such as "o2"
  - wn_begin: the starting wavenumber
  - wn_end: the ending wavenumber
  - comment: a space for notes about the table creation

- **Gas_[Q_{abs}]_Absorption** The absorption coefficients are a 4D table of size N_{pres} x N_{temps} x N_{vmrs} x N_{freqs} and are indexed in that order. The dataset attributes are:
  - addl_ident: a special identifier string, if any
  - gas_name: a string such as "o2", which should match its filename
  - comment: a space for notes
- **Gas_Index** a string containing the 2 digit HITRAN index of the principal absorbing gas, equivalent to Q_{abs} above.
- **Pressure** The pressure is a dataset of size N_{pres} representing the pressure in Pascals at each atmospheric level in the table
- **Temperature** Temperature is a 2D dataset of degrees Kelvin, of shape N_{pres} x N_{temps} It records the temperature grid point values, which might differ depending on pressure level.
- **Broadener_[Q_{brd}]_VMR** A dataset of size N_{vmrs} representing the different volume mixing ratios at which the foreign broadening gas is modeled. Q_{brd} is a HITRAN index. Now we only model H_2O broadening, so the index is always 01.

- broadener_name: the string “h2o”

- **Broadener_Index** a string contraining the 2 digit HITRAN index of the broadening gas, equivalent to Q_{brd} above
- **Wavenumber** The Wavenumber object is a dataset of size N_{freqs} describing the frequency grid spacing.

4 Remaining challenges and future directions

The goal for the OCO-2 mission is to achieve 1 ppm accuracy in the XCO2 retrievals. In order to allow room for other terms in the error budget, the aim is to achieve 0.1 % accuracy in the spectroscopic input to the forward model.

Figure 2, Figure 3 and Figure 4 show the magnitude of remaining residuals in the O_2 A band, the weak CO_2 band and the strong CO_2 band respectively. (Strictly speaking, the “current” residuals in these Figures are residuals using ABSCO v4.0. Residuals for ABSCO v4.2 are visually very similar, although the updates between v4.0 and v4.2 did result in small changes in the Level 2 retrieval results.) The differences between “previous” and “current” in these Figures are described in more detail in Thompson et al. (2012). All three bands show evidence of systematic spectral residuals with the current ABSCO version.

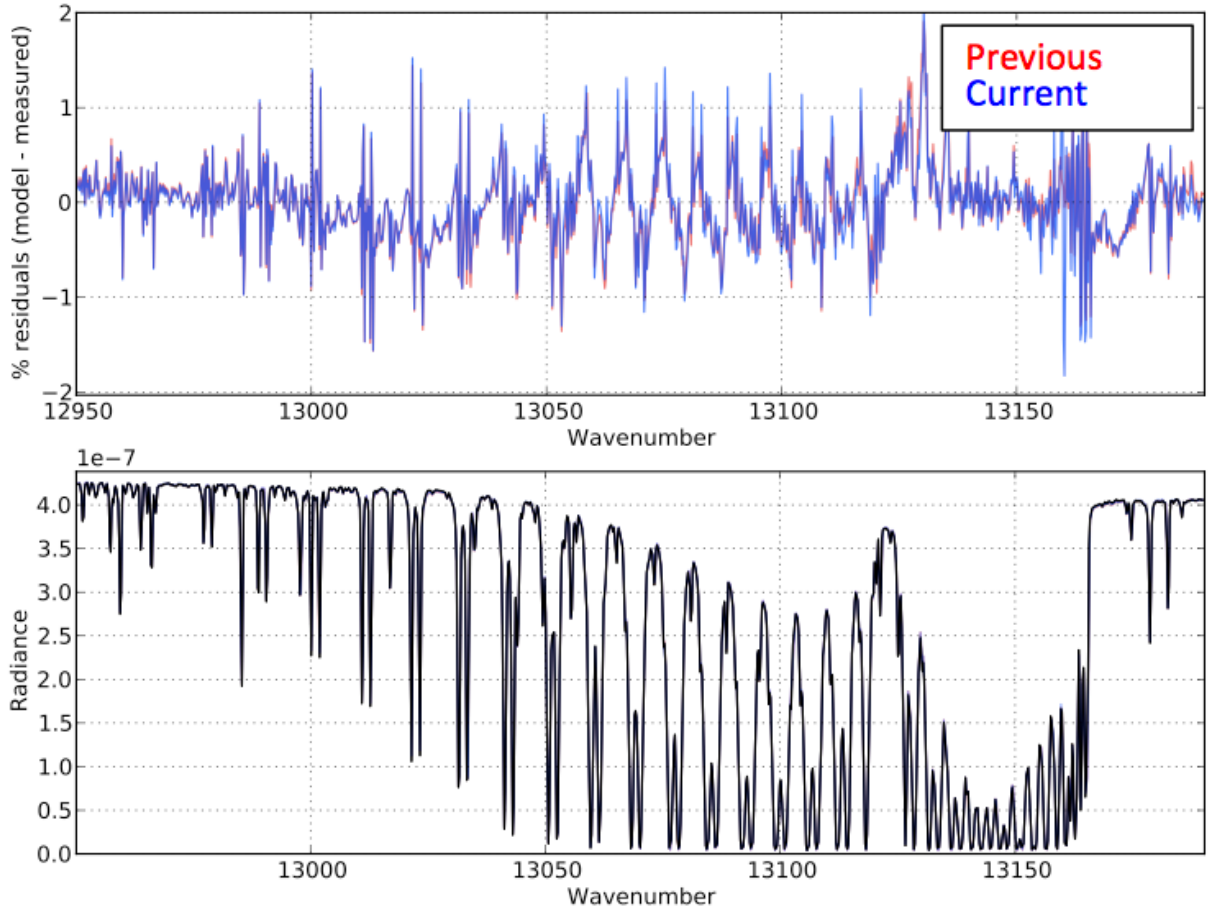

Figure 2. Averaged GOSAT residuals for the 0.76 µm O_2 A-band.

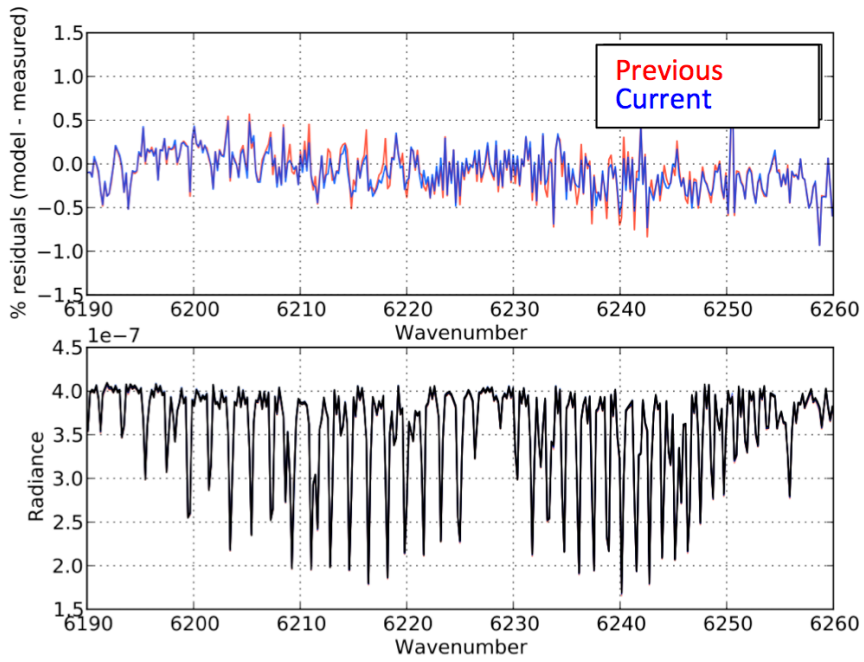

Figure 3. Averaged GOSAT residuals for the weak (1.6 µm) CO_2 band. (Figure from Thompson et al., 2012)

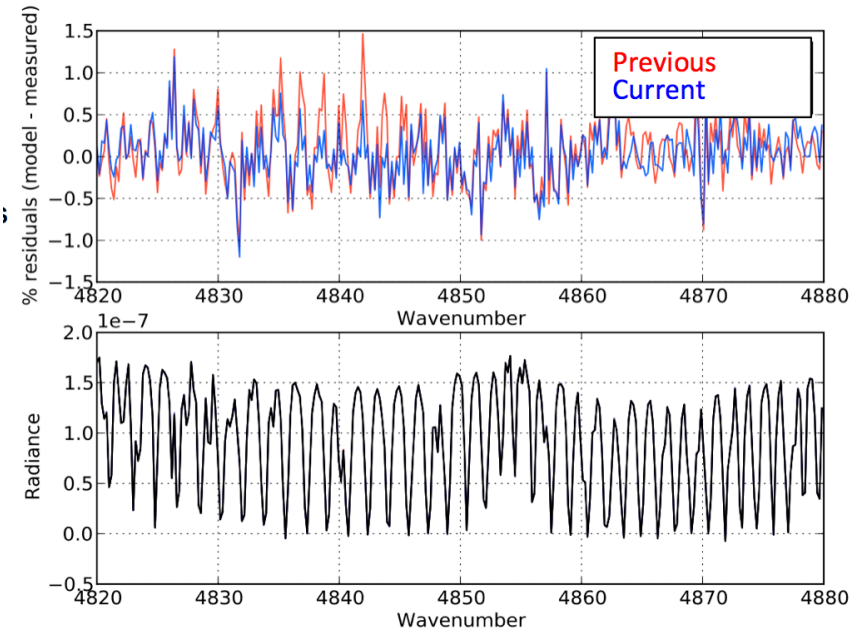

Figure 4. Averaged GOSAT residuals for the strong (2.06 µm) CO_2 band. (Figure from Thompson et al., 2012)

It has been shown (e.g. Thompson et al., 2012) that the traditionally used Voigt lineshape does not provide the required accuracy in this region. Research into the "best" lineshape is an ongoing

endeavor within the spectroscopy community. The approach taken by the OCO-2 ABSCO team has been to work towards simultaneous fitting of multiple laboratory spectra (Benner and Devi, 2011; Devi et al., 2007), where the laboratory conditions cover the full range of conditions encountered in Earth's atmosphere, in order to provide a consistent set of spectroscopic parameters for OCO-2.

Work is underway to apply the multi-spectrum fitting approach to FTS, CRDS and Photoacoustic Spectroscopy (PAS) measurements in the O_2 A band. The multi-spectrum fitting approach is expected to offer significant improvement over our current ABSCO version and to provide new insight into lineshape and collision-induced absorption (CIA) in the A band.

To date, this multi-spectrum fitting approach has been applied to room temperature Fourier Transform Spectrometer (FTS) laboratory measurements of CO_2 spectra. Resulting improvements in fits to atmospheric measurements are described in Thompson et al. (2012). However, the updated fits still do not allow us to fit available measurements within the noise. Work is underway to incorporate new cold temperature FTS measurements from JPL as well as Cavity Ringdown Spectroscopy (CRDS) measurements from NIST and Caltech into these fits. The new fits are expected to place further constraints on the spectroscopic parameters and lineshape in the OCO-2 CO_2 bands.

It will be necessary to continue to assess the need for laboratory measurements that can fill the gaps in our existing knowledge, to incorporate progress in theoretical studies into the multi-spectrum fitting approach and to continue to validate the ABSCO tables against high quality laboratory and atmospheric measurements (with various viewing geometries).

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